Scientific Research Publishing

Open Journal of Geology, 2025, 15(3), 142-154
https://www.scirp.org/journal/ojg
ISSN Online: 2161-7589
ISSN Print: 2161-7570

Petrography and Geochemistry of Manganese Protores from Laniokaha (Korhogo, Northern Côte d'Ivoire)

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How to cite this paper: Yao, A.N., Kouamelan, A.N., Houssou, N.N., Mondah, O.R., Gballou, C.B. and Coulibaly, Y. (2025) Petrography and Geochemistry of Manganese Protores from Laniokaha (Korhogo, Northern Côte d'Ivoire). *Open Journal of Geology*, **15**, 142-154.
https://doi.org/10.4236/ojg.2025.153006

Received: January 28, 2025
Accepted: March 15, 2025
Published: March 18, 2025

Abstract

The manganese protores of Laniokaha (Korhogo, Northern Côte d'Ivoire) are metamorphic rocks. Petrographic studies have identified three rock types: garnet amphibolite, garnet tephroitite, and gondite. These formations occur in succession within the same drilling profile. The minerals constituting garnet bearing amphibolite include amphibole, garnet, plagioclase, kaolinite, and opaque minerals. Garnet tephroitite is comprised of tephroite, garnet, calcite, plagioclase, and opaque minerals. Gondite is characterized by garnet, quartz, and opaque minerals. The manganese-bearing silicates identified are garnet and tephroite. Supergene alteration and enrichment of gondite led to the formation of hollandite and manganite. Manganese oxyhydroxides, manganite and hollandite were observed using metallographic microscopy. Scanning electron microscopy (SEM) revealed the presence of manganese carbonate kutnohorite in garnet tephroitite. The metals associated with manganese mineralization include pyrite, hematite, sphalerite, magnetite, goethite, gahnite, and rutile. These protores have high manganese contents ranging from 27% to over 38% Mn metal. Petrographic and geochemical characteristics indicate that these protores consist of silicate, oxyhydroxide, and carbonate minerals containing significant primary and secondary manganese mineralizations.

Keywords

Petrography, Geochemistry, Metallography, Manganese, Protores, Laniokaha, Côte d'Ivoire

1. Introduction

The Mn exploitation in Côte d'Ivoire began in 1960 with the Lauzoua deposit (south of Côte d'Ivoire) and lasted ten years. In 2012, the exploitation took place again on the same site and continues until today. Others few deposits have been discovered later but today only three are exploited in the northern part of Côte d'Ivoire: Bondoukou, Odienné and Korhogo. Recently, a company announced the discovery of an important deposit in the north of Côte d'Ivoire. At present, only the lateritic ore is exploited by the companies. Indeed, manganese protores of the Birimian volcano-sedimentary sequence in West Africa have historically been regarded as uneconomical deposits. These protores, formed through metamorphic recrystallization, are carbonates or silicates with stratiform mineralizations of low manganese content [1]. Studies on manganese in select West African regions, including Côte d'Ivoire, suggest that these protores attain economic significance only after supergene enrichment, similar to tropical regions of Africa, Brazil, or India [2]. Since then, manganese exploration in West Africa, particularly in Côte d'Ivoire, has largely focused on secondary oxidized ores [3]-[8]. In Côte d'Ivoire, the mined manganese ore has consistently been secondary oxides, resulting in limited data on primary, exploitable manganese protores.

This gap underscores the need to study protores in order to better understand the manganese mineralization they host.

The overarching objective of this study is to characterize the petrographic and geochemical properties of the manganese protores of Laniokaha (Korhogo, Northern Côte d'Ivoire). Specific objectives include:

i) Determine the petrographic nature of the protores;

ii) Characterize the manganese mineralization.

This research employs a range of analytical techniques, including petrographic thin-section analysis, scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS), X-ray diffraction (XRD), metallographic microscopy, and electron microprobe analysis. To quantify manganese content in both primary and secondary minerals, chemical analyses and mineral chemistry were also conducted. The results of this study provide new insights and directions for the exploration of manganese deposits in Côte d'Ivoire.

2. Geological Context

2.1. Geology of the Study Area

The Precambrian basement of Côte d'Ivoire is part of the Man Shield. To the west of this shield lies an Archean domain (3.6 - 2.5 Ga), separated from a Paleoproterozoic domain (2.5 - 1.8 Ga) to the east by the Sassandra Fault. The Paleoproterozoic domain is characterized by alternating greenstone belts and Birimian sedimentary basins, oriented NNE-SSW, and intruded by multiple generations of granitoids. This domain encompasses the study area, located in northern Côte d'Ivoire.

The geology of the Korhogo region has been described by Arnould (1960, 1961). It is predominantly composed of sedimentary formations, with metasiltstones being more abundant than meta-arenites. Gabbros, metagabbros, metadolerites, and amphibolites occupy the southwestern part of the area. In the northeastern and southeastern parts, outcrops include biotite granites, amphibole-bearing granites, monzogranites to monzonites, and biotite metagranites (**Figure 1**).

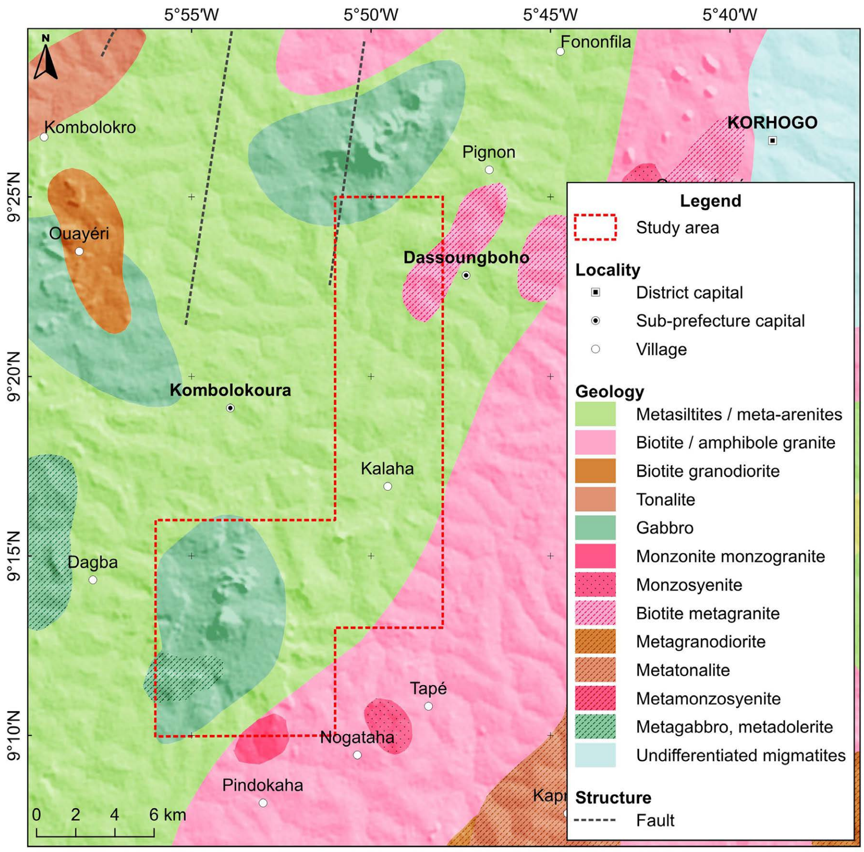


Figure 1. Geological map of the study area (excerpt from [9]).

2.2. Geology of the Laniokaha Deposit

The Laniokaha manganese deposit is located south of Korhogo. Discovered in 1953 by Arnould, it belongs to the manganiferous horizon of the Diaouala metamorphic series. This manganiferous horizon trends NNE-SSW and is bounded by two distinct zones: a highly metamorphic zone to the east, consisting of banded leptynites and schistose orthoamphibolites, and a less metamorphic zone to the west, characterized by schists, arkoses, and greenstones intruded by a series of small discordant massifs ranging from granite to gabbro emplaced at a later stage.

The Laniokaha deposit, of sedimentary origin, consists of two main zones of enrichment corresponding to two small elongated hills situated on a raised lateritic plateau. Initially deposited as manganiferous argillaceous sandstone, the deposit underwent folding, vertical repositioning, and general metamorphism, transforming into gondite. Lateritization further altered the deposit, producing a very dark, hard ore beneath the lateritic crust, between the surface and the water [10].

The deposit appears as stratified layers composed of gondite (spessartine quartzite), garnetite with or without amphibole, and free Mn oxides. The primary ores consist of uplifted spessartine quartzite beds interbedded with metamorphic schists [2]. The Laniokaha deposit contains low-grade, siliceous ores with an estimated tonnage of 1 million tons at 35% Mn [10].

The manganiferous horizon of Laniokaha lies between the banded leptynites of Mount Kafiplé to the east and the gabbros of the Sonloubakaha massif to the west. The leptynites of the Diaouala Birimian series exhibit a non-micaceous granitic appearance near the contact with the Korhogo granite massif. In contrast, the gabbros are homogeneous and display textures that range from fine-grained to coarse-grained or uralitized.

3. Sampling and Analytical Techniques

Rock core samples were collected during field missions. Thin sections of these rock cores were prepared in the litho-lamination workshop of the Geology, Mineral Resources, and Energy Laboratory at Félix Houphouët-Boigny University in Abidjan. The minerals and rock types were identified using a petrographic microscope. Scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS), metallographic microscopy, and electron microprobe analyses were employed to identify the manganese-bearing mineral phases. Certain minerals and mineralized phases were further characterized using X-ray diffraction (XRD) analyses.

Whole-rock geochemical analyses were conducted at Bureau Veritas Commodities Canada Ltd. The analytical method used was inductively coupled plasma atomic emission spectroscopy (ICP-AES) for the determination of major elements, including SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, TiO_2, MnO, P_2O_5, and loss on ignition (LOI) (**Table 1**).

Table 1. Major element composition of the manganese protores from Laniokaha in weight percent (% Wt) oxides.

Samples	Gondite	Garnet Tephroitite	Garnet Amphibolite
	C27	B42	A42
Major elements (% Wt)			
SiO_2	35.02	29.89	33.81
Al_2O_3	18.04	3.89	7.82
Fe_2O_3	4.50	3.62	5.26
MnO	35.16	50	42.78
MgO	0.97	3.82	3.82
CaO	3.77	1.49	2.12
Na_2O	0.06	0.02	0.03
K_2O	0.07	0.01	0.01
TiO_2	0.22	0.15	0.22
P_2O_5	0.12	0.02	0.02
LOI	1.17	1.19	0.42
Total	99.1	95	96.3

4. Results

4.1. Petrographic Data

The manganese protores in Laniokaha include gondite, garnet tephroitite, and garnet amphibolite (Figure 2).

- Gondite (C27)

The yellowish-gray gondite was sampled at a depth of −27 m, above the garnet tephroitite layer. It is massive with fine grain size (Figure 2(A)). Under the microscope, the rock exhibits a granoblastic texture and is mainly composed of garnet and quartz. Some opaque minerals are present in the fractures of the rock (Figure 2(B)). Garnet, occurring in automorphic form, is the most abundant mineral in the rock. Quartz grains, with bulging shapes, form the cement of the rock. The opaque minerals are often found as veinlets. The bulging shapes of the quartz grains are indicative of deformation within the rock. XRD analyses confirm this mineralogical composition (Table 2). The quartz and spessartine grains, which range from 0.1 to 0.4 mm in size, are inequigranular with rounded boundaries.

- Garnet Tephroitite (B42)

This gray-colored rock was observed at a depth of −40 m. It is compact with fine grain size (Figure 2(C)). Under the microscope, the rock displays a granoblastic texture with a preferential orientation of its minerals. These minerals include tephroite, garnet, plagioclase, calcite, and opaque minerals (Figure 2(D)). Tephroite, in a partially automorphic form, is the most abundant mineral. Garnet, which is automorphic, is also abundant, with zones of high concentration in the rock. Plagioclase, less abundant, sometimes alters to calcite. The opaque minerals occur in both automorphic forms and as veinlets. XRD analyses reveal, in addition to the minerals listed above, the presence of a few rare quartz crystals. The analyses identify the garnets as spessartine (Table 2). The mineral grains are inequigranular, ranging from 0.05 to 0.4 mm in size, with rounded boundaries. The minerals interlock, forming a dense texture.

- Garnet Amphibolite (A42)

The gray-colored amphibolite was sampled at a depth of −42 m. It is massive and has a fine grain size (Figure 2(E)). Under the microscope, the rock exhibits a granoblastic structure and is composed of amphibole, plagioclase, garnet, and opaque minerals (Figure 2(F)). Amphiboles are the most abundant minerals in the rock. Some show automorphic forms, while others are fractured due to deformation. Garnets are automorphic but less abundant. A few rare plagioclase crystals are also present. The opaque minerals appear as automorphic forms and veinlets within the rock. XRD analyses identified kaolinite and sodalite, in addition to the amphiboles, which were classified as tremolite amphiboles (Table 2). Weathering causes the rock to disintegrate into small blocks, during which amphiboles transform into opaque minerals, and plagioclase alters to kaolinite. The garnet and amphibole grains range in size from 0.1 to 0.6 mm.

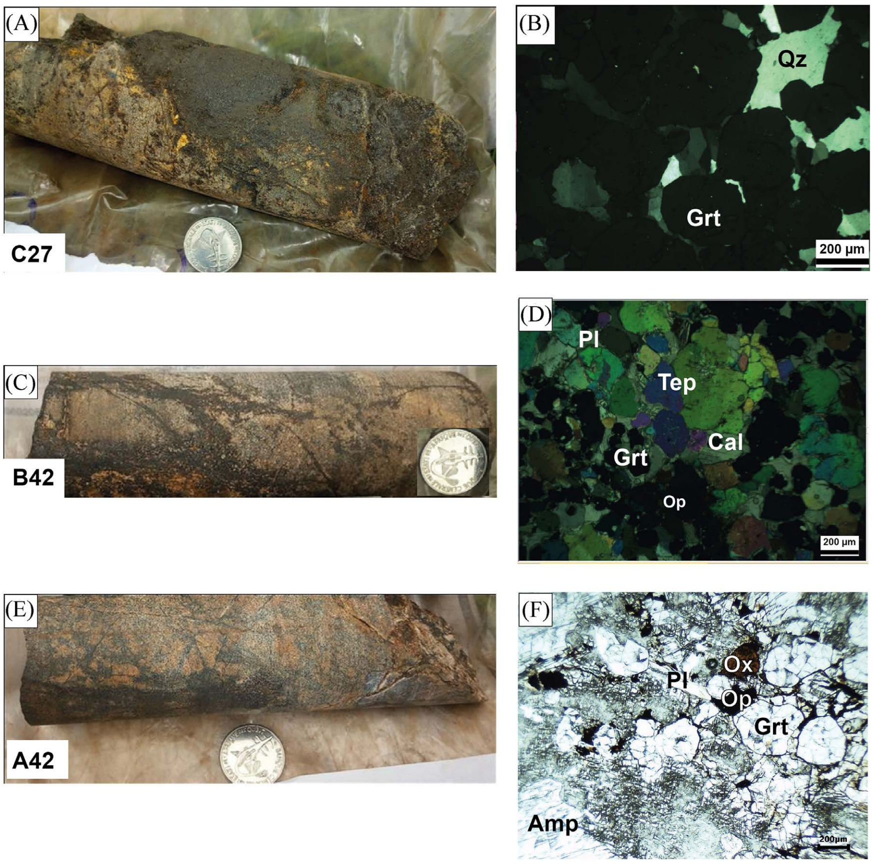


Figure 2. Appearance the manganiferous protores of Laniokaha. (A): Sample of the gondite; (B): Mineralogy of the gondite. (C): Sample of the garnet tephroitite; (D): Mineralogy of the garnet tephroitite; (E): Sample of the garnet amphibolite; (F): Mineralogy of the garnet amphibolite. Grt: Garnet; Qz: Quartz; Cal: Calcite; Op: Opaque; Ox: Oxide; Tep: Tephroite; Pl: Plagioclase.

Table 2. Mineralogical assembly of the protores determined by XRD analysis.

Samples	Protores					
	Gondite		Garnet Tephroitite		Garnet Amphibolite	
	Minerals	%	Minerals	%	Minerals	%
	Quartz	5.80	Spessartine	25.30	Tremolite	37.60
	Spessartine	92.20	Tephroite	68.80	Kaolinite	29.40
	Others	2	Sphalerite	1.40	Garnet	16.10
			Pyrite	1.20	Sodalite	10.60
			Others	5.30	Pyrite	2.60
					Others	3.7

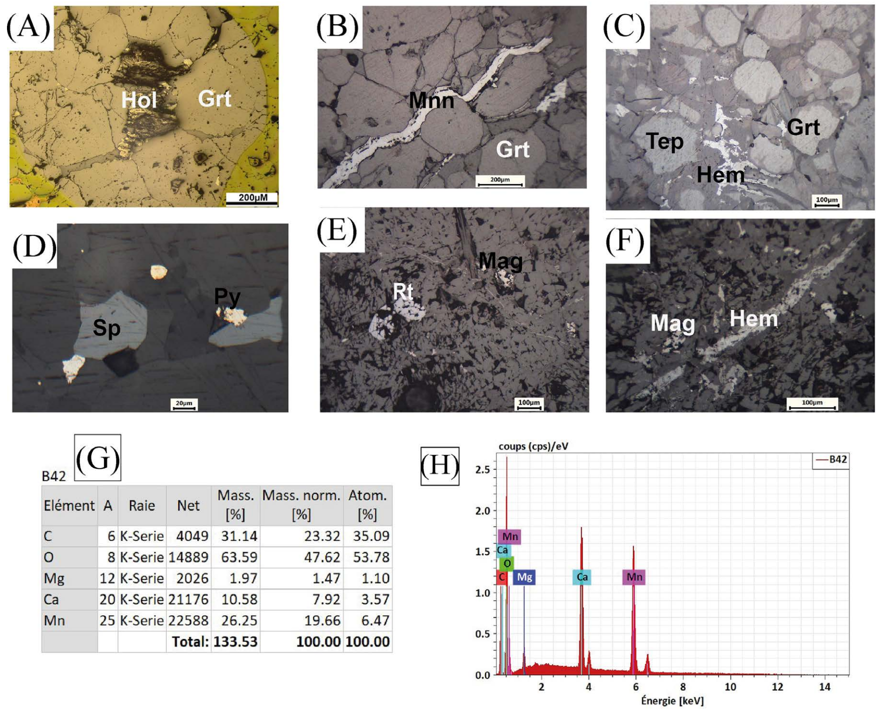
4.2. Description of Manganese-Bearing Mineral

4.2.1. Manganese Silicates

The manganese silicates identified are spessartine garnet and tephroite.

- Garnet

Garnets are common to all three protores studied. They exhibit automorphic forms and appear gray under reflected light (Figures 3(A)-(C), Figures 3 (E)). Analyses using XRD and electron microprobe characterize these garnets as spessartine garnets. The garnets in the gondite protolith show an average enrichment of approximately 26% Mn metal, based on electron microprobe analyses (Table 3).



Elément	A	Raie	Net	Mass. [%]	Mass. norm. [%]	Atom. [%]
C	6	K-Serie	4049	31.14	23.32	35.09
O	8	K-Serie	14889	63.59	47.62	53.78
Mg	12	K-Serie	2026	1.97	1.47	1.10
Ca	20	K-Serie	21176	10.58	7.92	3.57
Mn	25	K-Serie	22588	26.25	19.66	6.47
			Total:	133.53	100.00	100.00

Figure 3. The mineralised phases and associated metals of manganiferous protores under reflected light. (A): Hollandite and garnet in gondite. (B): Manganite and garnet in gondite. (C): Tephroite, garnet and hematite in garnet tephroitite. (D): Pyrite and Sphalerite. (E): Magnetite and rutile in garnet amphibolite. (F): Magnetite and hematite in garnet amphibolite. (G): SEM/EDS chemical analysis of kutnohorite. (H): SEM/EDS quantification of major chemical elements in kutnohorite. Hol: Hollandite; Grt: Garnet; Mnn: Manganite; Tep: Tephroite; Hem: Hematite; Sp: Sphalerite; Py: Pyrite; Rt: Rutile; Mag: Magnetite.

Table 3. Chemical composition of spessartine in percentage by weight of oxides.

Samples	Analysis by weight of oxides		
	Sps 1	Sps 2	Sps 3
Chemical composition (% Wt)			
SiO_2	36.36	36.93	35.53
Al_2O_3	20.77	20.09	18.87
MnO	33.36	32.81	33.24
FeO	3.49	4.34	4.56
CaO	4.19	4.19	4.99
MgO	1.19	0.92	0.57
Total	99.33	99.28	97.76

- Tephroite

Tephroite is colorless under reflected light (Figure 3(B)) and shows an average enrichment of 60.37% MnO, equivalent to approximately 47% Mn metal (Table 4). The metals associated with this mineralization include hematite, sphalerite, and pyrite.

Table 4. Chemical composition of tephroite in percentage by weight of oxides.

Samples	Analysis by weight of oxides					
	Tep1	Tep2	Tep3	Tep4	Tep5	Tep6
	Chemical composition (% Wt)					
SiO_2	30.81	30.57	31.02	30.91	30.74	30.71
FeO	2.55	2.67	2.51	2.53	2.75	2.60
MnO	60.28	59,70	61.27	60.02	60.32	60.64
MgO	5.57	5.45	5.37	5.39	5.34	5.51
NiO	0.23	0.26	0.05	0.17	0.28	0.12
Total	99.44	99.65	100.22	99.02	99.43	99.58

4.2.2. Manganese Oxyhydroxides

Hollandite and manganite are the manganese oxyhydroxides identified in the gondite protore.

- Hollandite

Hollandite results from the alteration of spessartine garnet and forms between garnet crystals. Under reflected light, it appears cream-white (Figure 3(A)) and contains an average of approximately 70.60% MnO, equivalent to ~55% Mn metal (Table 5).

Table 5. Chemical composition of hollandite in percentage by weight of oxides.

Samples	Analysis by weight of oxides		
	Oxide1	Oxide2	Oxide3
	Chemical composition (% Wt)		
SiO_2	0.07	0.40	0.07
Al_2O_3	0.13	0.10	0.16
MgO	0.02	0.11	1.72
CaO	0.37	0.57	0.46
FeO	0.06	0.76	1.95
MnO	74.8	71.05	65.96
NiO	0.00	0.12	0.28
BaO	0	2.3	1.67
K_2O	1.12	1.1	1.36
F	0	0.15	0.15
Cl^-	0.03	0.01	0.04
Total	76.60	76.67	73.82

- Manganite

Manganite appears gray-white under reflected light (**Figure 3(B)**). Manganese released from the spessartine garnet precipitated into a vein of the rock, forming this manganese oxyhydroxide. Its formation within the vein suggests a supergene origin.

4.2.3. Manganese Carbonates

Kutnohorite is the only manganese carbonate mineral identified in the garnet tephroitite protore.

- Kutnohorite

Scanning electron microscopy (SEM) analyses revealed the presence of the carbonate mineral kutnohorite, which is manganese-rich (~20% Mn) (**Figure 3(G)** and **Figure 3(H)**). The minerals associated with this mineralization include hematite, sphalerite and pyrite.

4.2.4. Metallic Parageneses

The identified metallic parageneses are as follows:

- Hollandite-manganite (**Figure 3(A)** and **Figure 3(B)**);
- Hematite-sphalerite-pyrite (**Figure 3(C)** and **Figure 3(D)**);
- Rutile-magnetite-hematite (**Figure 3(E)** and **Figure 3(F)**).

5. Discussion

5.1. Nature of Manganese Protores

Petrographic analysis of the manganese protores from Laniokaha identified three units of metamorphic formations: gondite, garnet tephroitite, and garnet amphibolite. Garnet is a mineral common to all three protores, while pyrite and plagioclase are present in both garnet tephroitite and garnet amphibolite. Similar protores have been observed in other manganese-bearing regions. For instance, [11] identified gondites in the Kisenge manganese deposit in the Democratic Republic of Congo. Gondite and tephroitite have also been reported in the Ziémougoula manganese deposit in Côte d'Ivoire [12]. According to [13], Proterozoic sedimentary manganese ores of the Gangpur series in Orissa, India, are of the gonditic type. Additionally, studies by [14] revealed that the protores of the northern Téra manganese deposit in western Niger are primarily gondites. Gondite has also been studied in the São João Del Rey mine in Minas Gerais, Brazil [15] [16].

5.2. Primary Mineralization

The analysis of mineralized phases has allowed us to identify the sources of primary manganese mineralization.

Primary manganese mineralization occurs in spessartine garnet, tephroite, and kutnohorite, which constitute the primary minerals of the protores. These minerals host manganese that was incorporated during their formation within the protores. The average primary manganese content in these minerals ranges from 20% to 46%, while the overall manganese content of the protores varies from 33% to 38%.

According to [2], manganese minerals in the protores of Côte d'Ivoire deposits are predominantly spessartine garnet, with kutnohorite identified as one of the primary oxides serving as a protore. Similarly, [17] noted that the protores of the Morro da Mina mine in Brazil are siliceous-carbonate rocks primarily composed of spessartine and tephroite. [6] described kutnohorite as one of the primary minerals in the carbonate protolith of the Tambao deposit in northern Burkina Faso. They also reported the presence of tephroite and spessartine at Tambao. The mineralised phases are more enriched in Manganese than the mineralised phases of Mn deposits in northern Guizhou, southern China considered to be the most economic spot due to what it contains such an industrially remarkable deposit [18]. The grades in the protores are also found in Ghana's most economical deposits [18].

5.3. Secondary Mineralization

Secondary mineralization in the gondite is characterized by the presence of hollandite and manganite, as illustrated in **Figure 3(A)** and **Figure 3(B)**. This mineralization primarily results from the enrichment of manganese oxides within the gondite. Spessartine garnet, which is unstable under supergene conditions, undergoes chemical alteration when interacting with meteoric water enriched in manganese. Although spessartine has a relatively low chemical weathering rate, its alteration leads to the formation of manganese oxyhydroxides such as hollandite and manganite [19].

Processes like hydrolysis, leaching, and oxidation facilitate the alteration of spessartine garnet, resulting in the deposition of hollandite and manganite in the gondite protore. These secondary oxyhydroxides are the primary hosts of supergene manganese mineralization, exhibiting an average manganese (Mn) content of approximately 55% (**Table 5**). In contrast, quartz remains unaltered due to its low dissolution rates under supergene conditions [20]. Weathering contributed to the enrichment of manganese ore. The primary supergene mineral assemblage comprises quartz, garnet, hollandite, and manganite. The occurrence of hollandite and manganite in supergene environments has been widely documented by several studies [6] [18] [21]-[23]. Additionally, other researchers have explored the transformation of spessartine garnet into manganese oxyhydroxides under supergene settings [2] [14] [15]. The average Mn content of approximately 55% in the manganese oxides from Laniokaha is notably higher than the 34.4% reported by [23] for the Mn oxides in gondites from the Xialei deposit in China. Furthermore, hollandite from Laniokaha demonstrates a higher manganese content than some minerals (19%) from the manganese deposits in northern Guizhou, southern China, which are regarded as highly economic due to their industrial significance [18]. Similarly, the Nikopol manganese deposits in southern Ukraine, which are considered globally significant, have an average major oxide content of 40.7% MnO (equivalent to 31% Mn) [18]. This value is lower than the average Mn content (~55%) observed in hollandite from Laniokaha.

6. Conclusions

The manganese protores of Laniokaha are silicate and silico-carbonate metamorphic rocks with significant manganese mineralization potential. The garnet amphibolite comprises tremolite, kaolinite, spessartine, sodalite, pyrite, plagioclase, hematite, magnetite, and rutile. The garnet tephroitite consists of spessartine, tephroite, plagioclase, calcite, sphalerite, pyrite, and hematite. The gondite is composed of spessartine, quartz, hollandite, and manganite. A common feature across all three protores is the presence of spessartine garnet.

Manganese mineralization is hosted within silicates, oxyhydroxides, and carbonates in these protores. Key manganese-hosting minerals include garnet (~26% Mn), tephroite (~46% Mn), manganite, hollandite (~55% Mn), and kutnohorite (~20% Mn). Primary mineralization is associated with silicates (spessartine, tephroite) and carbonates (kutnohorite), whereas secondary mineralization is hosted in oxyhydroxides (manganite and hollandite), formed through the alteration of spessartine garnet. Notably, the gondite protore hosts both primary and secondary mineralization. The manganese grades of these protores—gondite (~27% Mn), garnet tephroitite (38% Mn), and garnet amphibolite (~33% Mn)—are comparable to grades from economically significant manganese deposits in China, Ukraine, and Ghana, which are known for their impact on the global manganese market.

Petrographic and geochemical analyses of the manganese protores in Laniokaha highlight their potential for future exploration and exploitation. These findings open new avenues for manganese exploration in Côte d'Ivoire, particularly by targeting protores as promising sources of manganese mineralization.

Acknowledgements

Our thanks go to PASRES for funding this research and to the Félix Houphouët-Boigny University for hosting it. We also thank the Shiloh Manganese Company for their technical, financial and moral support and the accessibility of their property for field work.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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